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1993 J. Phys.: Condens. Matter 5 L349

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LETTER TO THE EDITOR

Dynamics and effective thermodynamics of a model structural glass

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Abstract. We use Monte Carlo methods to investigate a purely dynamical model for structural glasses. We observe stretched exponential decays of the equilibrium autocorrelation function and measure the late-time relaxation times τ . These diverge with temperature following a Vogel–Fulcher law. We also study systems which are quenched deeply and then re-heated. This gives a peak in the effective specific heat with properties matching those of the glass transition. The model thus reproduces the main phenomenology of glasses and the glass transition.

It is thought that structural glasses are not equilibrium phases but are materials trapped in long-lived metastable states. However, the mechanism by which this trapping occurs is not known, as is how its onset near a glass can give rise to non-exponential decays of autocorrelation functions, and to a divergence in the relaxation time at a non-zero temperature. In addition it is not obvious how such a purely dynamical outlook can yield the first-order-like thermal properties of the glass transition. Given these difficulties much effort has been devoted to developing a well-defined dynamical model which reproduces these phenomena.

In this Letter we present a purely dynamical model for structural glasses that tests the idea of local frustration as the relevant microscopic mechanism. This is a simplified version of the facilitated kinetic Ising model of Fredrickson and Andersen (FA) [?, ?]. Here we reconsider this idea in both two and three dimensions, generating results with improved statistics and examining the effective thermodynamics upon heating and cooling. At low temperatures the equilibrium autocorrelation functions have the late-time stretched exponential decays characteristic of glass-forming materials. More importantly we can use these data to measure the late-time temperature-dependent relaxation times τ . In all cases that our data are best represented by a τ which diverges at a non-zero temperature following a Vogel–Fulcher (VF) law. Lastly, our simulations of heating and cooling of a quenched low-temperature ‘glass’ show a peak in the effective specific heat with properties very similar to those of experimental glass transitions. Thus this model is able to reproduce much of the phenomenology of glassy relaxation and the glass transition, with no adjustable parameters.

We emphasize that our model is an extremely simple spin model for the glass transition, with built-in dynamic frustration. As such, it differs fundamentally from molecular models for structural glasses (which can be based on, for example, the detailed molecular interactions in a binary alloy). Nevertheless, the present model leads to long-time behaviour which bears similarities with the more realistic models, thereby suggesting that the long-time features of stretched exponential decay and a VF law may be intrinsically dynamical phenomena.

The phenomenology of glasses has been extensively reviewed [?], so we shall only summarize results. The glass transition temperature T_g is operationally defined as the point where the measured viscosity exceeds 10^{13} P or where the specific heat shows a prominent peak [?]. The value T_g is also known to depend on the time scale of the measurement. Near to and above T_g glass-forming materials show non-exponential decays in autocorrelation functions that at late time are often described by $C(t) \sim e^{-(t/\tau)^\alpha}$ with α , a non-universal quantity, being < 1 . The relaxation time τ grows rapidly with decreasing temperature as the glass transition is approached, and in many cases appears to diverge at a temperature T_0 via $\tau \sim e^{A/[k(T-T_0)]}$, known as the Vogel–Fulcher (VF) law when $T_0 > 0$. Most glass-forming materials, such as polymers, metallic glasses and ionic systems show this non-Arrhenius relaxation near the glass transition, with $T_0 < T_g$.

The physical origin for these phenomena largely remains an open question, and has been investigated by techniques as varied as hydrodynamic mode-coupling theories [?], structural [?], hierarchical [?] and free-volume [?] models. None of these, however, is thought to provide a complete picture of glasses. One idea common to many of these is that dense local packing leads to dynamical frustration, with long-timescale/lengthscale relaxation requiring cooperative relaxation on all shorter times/lengths. Our intent is to test this explicitly.

Direct simulation of glasses has been performed by molecular dynamics (MD) [?]. This is difficult, owing to the large timescale difference between the motion of the individual particles and the much slower structural relaxation of glassy materials. Nevertheless, such work shows evidence for stretched exponential decays of particle self-correlation functions and for non-Arrhenius divergence of the relaxation times [?,?]. However, the data are generally not of sufficient quality to verify or refute the VF form. Work on deep quenches has verified the importance of local barriers in slowing the relaxation, but it is difficult to determine, on this basis alone, whether these barriers are the sole mechanism of glassy relaxation.

The facilitated kinetic Ising model of FA [?,?] provides a quite different simulation approach, allowing one to investigate whether dynamical frustration is responsible for glassy phenomena within the framework of the well understood Ising model. However, earlier numerical work in two dimensions found only weak evidence for divergence of the relaxation time at non-zero temperatures, although it did show a stretched-exponential decay of the autocorrelation function [?].

In this Letter we revisit this idea using a simple variant of the FA model. Following FA we begin with an Ising model with site spins $S_i = \pm 1$. We also consider the model in the *absence* of any site-site coupling ($J = 0$), but in the presence of an external field h (for convenience we set $h \equiv 1$ and define a positive field as being in the negative spin direction). The Hamiltonian is then simply $\mathcal{H} = \sum_i S_i$, so that there is no underlying thermodynamic transition. In the absence of dynamical frustration the equilibrium and non-equilibrium properties on the model are well known. All autocorrelation or relaxation functions decay exponentially with time and the equilibrium average spin $m_0 = \langle S \rangle = -\tanh(1/kT)$.

We add dynamical frustration (facilitation) by allowing a spin to attempt a flip (with standard Boltzmann probability) *only* if the spin is surrounded by a ‘sufficient’ number of up spins. This is equivalent to having no energy barrier for a move surrounded by ‘sufficient’ up spins, and an infinite barrier otherwise. There can be many such rules. We define a 2-site facilitation rule as one where a flip is allowed only if two or more of the nearest-neighbours’ spins are in the spin-up state, and so on. The kinetics of this model are easily implemented within Metropolis Monte Carlo dynamics by adding the facilitation rule to the transition probabilities, giving

$$P_{a \rightarrow b} = f(\{S_j\}) \begin{cases} e^{-(E_a - E_b)/kT} & E_a < E_b \\ 1 & E_a \geq E_b \end{cases} \quad (1)$$

where $E_a = -S_i$ and $E_b = S_i$ are the energies at site i (initially with spin S_i) before and after the attempted flip, respectively. The facilitation function $f(\{S_j\})$ depends only on the states of the spins $\{S_j\}$ neighbouring the site of interest, and is either 1 or 0 depending on whether or not there are sufficient neighbours to satisfy the facilitation rule [?]. The effect of this rule is to slow the dynamics such that the equilibrium thermal averages are preserved, unless a true dynamical transition has occurred.

The model was investigated via a multi-spin kinetic Ising model algorithm presented previously [?, ?]. In two dimensions we examined 2-site facilitation and in three dimensions studied both 2- and 3-site models. We performed two studies of the facilitation models, the first on systems at equilibrium, the second on systems frozen into a glass phase. To prepare an equilibrium system we began with an all spin-up system, quenched it under a fixed external field $1/kT \equiv \beta$ and monitored the evolution of the average magnetization $m(t) = \langle S \rangle$ as the system evolved to equilibrium. At late times $m(t)$ reaches the equilibrium value $m_\infty = \lim_{t \rightarrow \infty} m(t)$. For sufficiently large system sizes $N = L^d$ we find $m_\infty(N) \equiv m_0$: i.e. the equilibrium average is equal to that predicted by the equilibrium partition function. As noted previously [?], facilitation can trap the system within a restricted configuration space if the quench field is too deep for a given system size. In this case $m_\infty > m_0$. We used this criterion to detect finite-size effects in our simulations, and accordingly increased system sizes to give correct results. Provided $m_\infty \approx m_0$ other quantities we measured, in particular the relaxation times, were independent of the size of the system. In two dimensions these criteria implied sizes from $L = 24$ to 48, and in three dimensions $L = 8$ to 16.

The important equilibrium quantity is the spin autocorrelation function $\Phi(t) = (\langle S_i(t)S_i(0) \rangle - m_\infty^2)/(1 - m_\infty^2)$, where the average $\langle \dots \rangle$ is over all sites. To ensure reliable late time estimates the averages were taken over upwards of 640 independent runs.

In figure 1 we plot characteristic results for the equilibrium autocorrelation functions, shown here for a three-dimensional system with the two-site facilitation rule. At low temperatures (high fields) the late-time behaviour is well described by a stretched exponential, with the stretch slope α decreasing with decreasing temperature [?]. We fit the late-time data to the function $e^{-(t/\tau)^\alpha}$ to determine the stretch power α and relaxation time τ . To test the appropriateness of this form we also fit the data to a sum of exponentials $Ae^{-t/\tau_1} + (1 - A)e^{-t/\tau_2}$, and compared the quality of the fits. In general the two-parameter stretch form represented the data better than the three-parameter sum of exponentials.

Figure 2 shows the temperature dependence of the fitted relaxation times. All our results are concave upwards, indicating divergence at a non-zero temperature. We fit these data to two possible forms for this divergence, a power law and the VF expression, and have summarized the results in table 1. It is clear that the VF expression provides a much better fit to the data. Thus we have shown, for the first time, that a microscopic, purely dynamical model can give rise to this aspect of glassy phenomenology.

In our second study we investigated the thermal properties of the model by quenching a system below the divergence temperature, relaxing it into a 'glassy' state, and then heating it, measuring the average energy per spin $\langle E \rangle$ and fluctuations $\langle E^2 \rangle - \langle E \rangle^2$. An effective specific heat per spin can be obtained in two ways: by differentiating $C_V/Nk = d\langle E \rangle/dT$ or by the statistical expression $C_V^{\text{eff}}/Nk = (\langle E^2 \rangle - \langle E \rangle^2)/(kT)^2$. These expressions are not equivalent for the non-equilibrium situations considered here. The former will reflect the thermal properties that would be measured in an experiment, most importantly in the low-temperature region where ergodicity is broken on the simulation timescale. These results

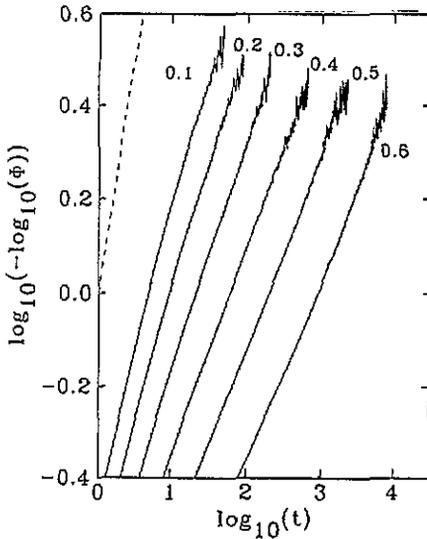


Figure 1. (Log-log)-log plot of the autocorrelation function Φ as a function of time t for different inverse temperatures β . These results are for a three-dimensional system and the 3-site facilitation rule. Straight lines imply a stretched-exponential, the slope being the stretch power α . The dashed line corresponds to exponential decay $\alpha = 1$.

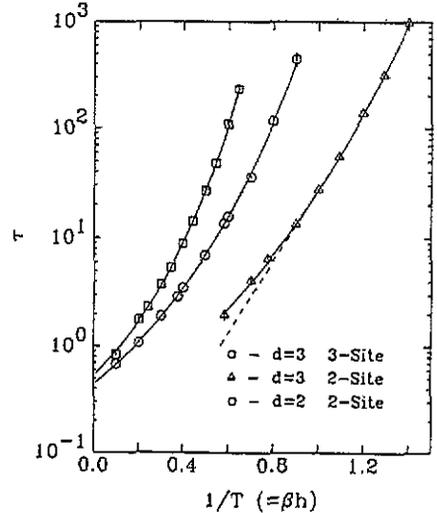


Figure 2. Plot of the relaxation times as a function of inverse temperature β for the three cases studied. A straight line would correspond to Arrhenius relaxation. The concave upwards curves indicate divergence of the relaxation time at non-zero temperatures. The solid lines are VF fits using the parameters from table 1. The dashed line gives a best fit for a power law.

Table 1. Results from fitting power-law and VF expressions to the relaxation time data shown in figure 2.

Dimension d	Facilitation rule	C	A	kT_0	χ^2/df
VF $\tau = Ce^{A/(kT - kT_0)}$					
2	2-Site	0.43 ± 0.02	4.2 ± 0.1	0.50 ± 0.03	2.3
3	2-Site	0.16 ± 0.02	3.56 ± 0.14	0.30 ± 0.01	2.1
3	3-Site	0.51 ± 0.02	5.2 ± 0.2	0.68 ± 0.03	1.8
Power law $\tau = A(kT - kT_0)^{-\gamma}$					
2	2-Site	5.3 ± 0.5	1.3 ± 0.1	1.18 ± 0.05	118
3	2-Site	1.8 ± 0.1	3.2 ± 0.1	0.57 ± 0.01	7.9
3	3-Site	50 ± 133	2.8 ± 1.7	0.72 ± 1.06	264

can be contrasted with the exact solution in the absence of facilitation.

Results for a typical heating and cooling run for the two-dimensional 2-site facilitation model are shown in figure 3. This system was initially quenched from the all spin-up state to $kT = 0.45455$ ($\beta = 2.2$), and allowed to relax for 8×10^6 mcs (1 mcs \equiv 1 MC step per spin). It was then heated (and subsequently cooled), at a constant rate of 1×10^{-5} kT MCS $^{-1}$. This initial temperature is below the predicted kT_0 of this system (see table 1) so the relaxation time of the prepared 'glassy' state is extremely long: in particular no noticeable change in properties would occur over the time scale of the heating/cooling runs.

Ergodicity, on the simulation timescale, appears to break down just below $kT = 3.0$ for heating and $kT = 2.0$ for cooling. The heating run shows a large peak in the 'effective' specific heat C_V/Nk , while the subsequent cooling run shows a much smaller and broader peak centred at a slightly lower temperature. If we reduce the scanning rate dT/dt the large peak narrows and moves to lower temperatures, while the broad cooling peak is largely unchanged (results not shown). This 'hysteresis' upon heating and cooling and the

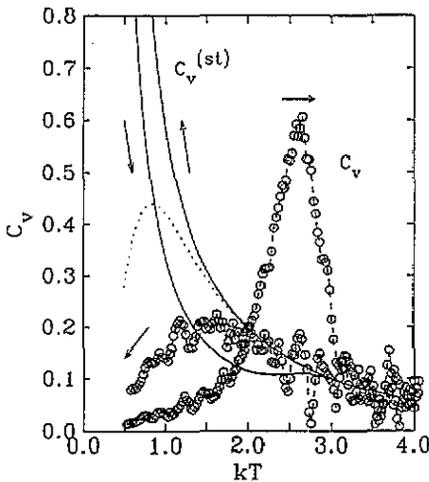


Figure 3. Effective specific heat as a function of temperature for a system heated from $kT = 0.45455$ to $kT = 6$ and then cooled at a rate $k|dT/dt| = 5 \times 10^{-4}$ kT MCS^{-1} . The arrows indicate the direction of the temperature change. The solid line gives the 'statistical' specific heat C_v^{st} defined in the text, while the open symbols linked by the dashed line give $C_v/Nk = d(E)/dT$. The dotted line is the exact result in the absence of facilitation. The large 'glass' transition peak is clearly evident, as is the breakdown of ergodicity for $kT \leq 2$ on cooling and $kT \leq 3$ on heating.

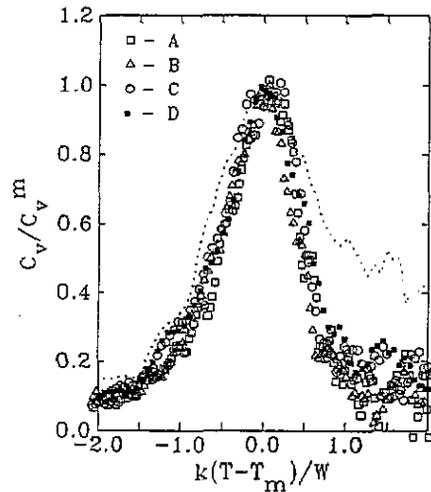


Figure 4. Scaling plot for the glass transition. The data have been scaled via $(kT - kT_m)/W$, C_v/C_v^m , where T_m is the mid-point of the peak, W is the peak full-width at half-maximum and C_v^m is the peak height. The heating rates for the different curves are: (a), 1×10^{-3} kT MCS^{-1} ; (b), 5×10^{-4} kT MCS^{-1} ; (c), 2×10^{-4} kT MCS^{-1} ; and (d), 1×10^{-4} kT MCS^{-1} . The dotted line (which does not scale) is the scaled result for systems heated at the very slow rate 5×10^{-6} kT MCS^{-1} . In this case the 'glass transition' peak is centred at $kT = 1.25$, where the equilibrium specific heat is large (see the dotted line in figure 3).

dependence of the peak position on dT/dt are commonly observed with real glasses [?]. The calorimetric behaviour thus possesses the characteristic phenomenology of the glass transition. We stress that this peak arises for purely dynamical reasons and that there is no underlying thermodynamic transition.

The quantity C_v^{st} (solid line in figure 3) tells us about the microscopic ramifications of the broken ergodicity associated with this peak. Since this diverges at low temperatures $\langle E^2 \rangle - \langle E \rangle^2$ does not go to zero as $T \rightarrow 0$. This means that fluctuations are quenched-in, on the timescale of the simulation, in keeping with dynamical arguments for glassy behaviour.

Lastly we attempted to scale the curves for different heating rates by the standard scaling form, with results shown in figure 4. Provided the non-equilibrium peak is well displaced from the broad background peak of the equilibrium model the data scale very well. This ceases to be the case (dotted line) when a large portion of the specific heat is due to the equilibrium background peak.

In conclusion, we have demonstrated that stretched exponential decays of the equilibrium autocorrelation functions, dependence of the stretch power α on temperature, Vogel-Fulcher divergences of the associated relaxation times and the qualitative behaviour of the glass transition can all arise from a purely dynamical model. This is strong evidence that the glass transition has its origin in dynamical frustration. We also found scaling of the non-equilibrium specific heat over a wide range of heating rates. We have also examined the dependence of the glass transition on the annealing time of the low-temperature glass and are examining the behaviour of the model to other experimental protocols. These results will be reported in a forthcoming paper.

We wish to thank Drs K Elder, R Brüning and L Lewis for useful discussions. This work was supported by the Natural Sciences and Engineering Research Council of Canada, le Fonds pour la Formation de Chercheurs et l'Aide à la Recherche de la Province de Québec.

References

- [1] Fredrickson G H and Andersen H C 1984 *Phys. Rev. Lett.* **53** 1244
Fredrickson G H and Andersen H C 1985 *J. Chem. Phys.* **83** 5822
- [2] Fredrickson G H and Brawer S A 1985 *J. Chem. Phys.* **84** 3351
Hakanishi H and Takano H 1986 *Phys. Lett. A* **115** 117
- [3] McKenna G B 1984 *Comprehensive Polymer Science Vol 2: Polymer Properties* ed C Booth and C Price (Oxford: Pergamon)
Spaepen F and Turnbull D 1984 *Ann. Rev. Phys. Chem.* **35** 241
- [4] Brüning R private communication
Moynihan C T, Opalka S M, Mossadegh R, Crichton S N and Bruce A J 1988 *Molecular Dynamics and Relaxation Phenomena in Glasses* ed Th Dorfmueller and G Williams (Berlin: Springer)
Gronert H W, Gillissen F and Herlach D M 1988 *Mater. Sci. Eng.* **97** 191
Moynihan C T, Eastal A J, Wilder J and Tucker J 1974 *J. Phys. Chem.* **78** 2673
- [5] The idea of a hydrodynamic model for the liquid-glass transition was first put forward by Leuthesser D 1984 *Phys. Rev. A* **29** 2765
Most recently this approach has found success in describing the properties of viscous supercooled fluids. Some recent reviews are:
Götze W 1992 *Liquids, Freezing and the Glass Transition* ed D Levesque, Hansen J P and Zinn-Justin J (New York: Elsevier)
Kim B and Mazenko G F 1992 *Phys. Rev. A* **45** 2393
- [6] Jäckle J 1987 *Philos. Mag.* **B 56** 113
Jäckle J, Stinchcombe R B and Cornell S 1991 *J. Stat. Phys.* **62** 425
Palmer R G 1984 *Cooperative Dynamics in Complex Physical Systems* ed H Takayama *Springer Series in Synergetics, Vol. 43* (Berlin: Springer)
- [7] Palmer R G, Stein D L, Abrahams E and Anderson P W 1984 *Phys. Rev. Lett.* **53** 958
- [8] Turnbull D and Cohen M H 1961 *J. Chem. Phys.* **34** 120
The approach has been applied to the glass transition. See
Cohen M H and Grest G S 1979 *Phys. Rev. B* **20** 1077
Grest G S and Cohen M H 1980 *Phys. Rev. B* **21** 4113
- [9] Recent reviews are
Barrat J-L and Klein M L 1991 *Ann. Rev. Phys. Chem.* **42** 23
Angell C A, Clarke J H R and Woodcock L V 1981 *Adv. Chem. Phys.* **48** 397
Frenkel D and McTague J P 1980 *Ann. Rev. Phys. Chem.* **31** 491
The former examines MD as a test of mode-coupling theory.
- [10] Pastore G, Bernu B, Hansen J-P and Hiwatari Y 1988 *Phys. Rev.* **38** 454
- [11] In the FA model the function f depends on the number of neighbouring up spins m_j ; e.g. $f \sim \frac{1}{2}m_j(m_j - 1)$ for their 2-site model. Thus the flipping probability is weighted by the number of up spin neighbours. By choosing $f = \{0, 1\}$ we preserve the essence of the model—that spins with insufficient up-spin neighbours cannot evolve—and have simplified the microscopic dynamics for those which do evolve. The advantage is that the extrapolation to a 0-site rules yields the kinetic Ising model.
- [12] Graham I S and Grant M *Preprint*
- [13] Bhanot G, Duke D and Salvador R 1986 *J. Stat. Phys.* **44** 985
Roland C and Grant M 1989 *Phys. Rev. B* **39** 11971
- [14] We chose the stretch form as it well represented our late-time data. This has also been seen in dielectric data, e.g.
Dixon P K, Wu L, Nagel S R, Williams B D and Carini J P 1990 *Phys. Rev. Lett.* **65** 1108
although there is now some controversy over this. See
Sch Aönhlas, Kremer F and Schlosser E 1991 *Phys. Rev. Lett.* **67** 999
Other forms have been proposed. See,
Davidson D W and Cole R H 1951 *J. Chem. Phys.* **19** 1484